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ABSTRACT

The present work investigates the photocatalytic degradation efficiency of biorecalcitrant macrolide antibiotics in a circulating tubular photoreactor. As target pollutants, spiramycin and tylosin were considered in this study. The photoreactor leads to use an immobilized titanium dioxide on non-woven paper under artificial UV-lamp irradiation. Maximum removal efficiency was achieved at the optimum conditions of natural pH, low pollutant concentration and a 0.35 L min^{-1} flow rate. A Langmuir-Hinshelwood (L-H) model was used to fit experimental results and the model constants were determined. Moreover, the total organic carbon analysis reveals that spiramycin and tylosin mineralization is not complete. In addition, the study of the residence time distribution allowed us to investigate the flow regime of the reactor. Electrical energy consumption for photocatalytic degradation of macrolides using circulating TiO_2-coated paper photoreactor (CTCPP) was lower comparing to some reported photoreactors used for the elimination pf pharmaceutic compounds. A repetitive reuse of the immobilized catalyst was also studied in order to check its photoactivity performance.

Keywords: flow regime, immobilized catalyst, Langmuir-Hinshelwood model, photocatalytic degradation, photoreactor, waste water.

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INTRODUCTION

In recent years, recalcitrant organic pollutants (ROPs) in the aquatic environment, such as antibiotics, have attracted an increasing attention due to their nature and impacts on human health and environment (Heberer, 2002; Michael et al., 2013). Their presence and accumulation in natural waters are considered as an emerging pollution problem, leading to the disruption of the ecosystem, the increased malfunction in the reproduction of aquatic species (Heberer, 2002) and possible risks to human health (such as allergies, endocrine disruption and damages to the central nervous system) through drinking water and/or food-chain (Kümmerer, 2000).

Conventional biological treatments have proved to be inefficient for the removal of antibiotics because of their complex molecular structure, high toxicity and poor biodegradability (Kümmerer, 2000). Indeed, these processes were not designed to eliminate such kind of pollutants. Oxidative processes appear to be efficient for the treatment of waste waters containing pharmaceuticals (Doll and Frimmel, 2005). Among them, heterogeneous photocatalysis has emerged as a promising technique for the transformation, deactivation and minimization of persistent organic compounds in water (Doll and Frimmel, 2005). Such process uses semiconductor which is activated under ultraviolet radiation, allowing the generation of highly reactive free $OH^{\bullet}$ radicals. Among the various solids, titanium dioxide TiO_2 is largely employed because of its low cost and photo-stability (Schiavello, 1988).

Several studies have focused on the chemical pathways or degradation kinetics of the process, but there have been only few reports on the design of photocatalytic reactors (Sahle-Demessie et al., 2003). Reactor geometry is also a key factor in liquid-phase photocatalysis which influences the photodegradation efficiency (Paz, 2009). Photoreactor scale-up is a major challenge in photochemical reaction engineering using advanced oxidation process (AOP) technologies for the degradation of ROPs in water (Ghafoori et al., 2014). Using tubular reactor in this work, the main operating parameters such as initial pollutant concentration, pH and the flow rate can be optimized. An immobilized titanium dioxide (TiO_2-coated paper) was employed due to the practical interest of reactors operated with immobilized semiconductors (Gholami et al., 2012; Li et al., 2015). Indeed, the use of immobilized catalyst permits to avoid tedious separation step of the particles (Merabet et al., 2009) and its reuse. In addition, residence time distribution (RTD) studies were conducted in order to investigate the effect of the flow rate on pollutant removal efficiency.

Two macrolide antibiotics have been studied in this work: spiramycin (SPM) and tylosin (TYL). Their widespread usage and frequent detection in the aquatic environment highlights the need for their removal. According to recent studies, SPM is one of the most abundant macrolide antibiotic detected in wastewaters (Michael et al., 2013). Its concentration in the effluent of Sewage Treatment Plants has been detected to values up to 0.6 ng L^{-1}. SPM is generally prescribed in the treatment of different types of infections as toxoplasmosis and protozoan infections (Civitareale et al., 2004). TYL is an antibiotic which represents 13% of the detected drugs. Its detection limit in wastewater is about 0.01 mg L^{-1} (Huang et al., 2001). TYL is a fermentation derived macrolide antibiotic, which inhibits protein synthesis of specific bacterial species (Elanco, 1982). It is used as feed additive in order to modulate gut microbial flora, thus enhancing the growth rates performances in calves, cattle and poultry.

The information dealing with the removal of these two antibiotics by heterogeneous photocatalysis is scarce. Up to our knowledge, no works have been reported on the removal of SPM and TYL by using a tubular photoreactor with immobilized TiO_2.

The overall aim of this work was to (i) investigate at a pilot scale the effect of some operating parameters on the degradation of target compounds and check the coherence of experimental results with L-H kinetic model; (ii) assess the mineralization of the parent molecules at the end of the reaction process; (iii) investigate the flow regime inside the reactor for different flow rates via residence time distribution (RTD) curves; (iv) evaluate the electrical consumption of the photoreactor system by the determination of electrical energy per order and (v) check the photoactivity performance of the immobilized catalyst over nine cycles.

MATERIALS AND METHODS

Chemicals

Spiramycin (purity of 98%) was kindly offered by Sanofi-Aventis Company for Pharmaceutical Industry (Algeria), and tylosin tartrate was obtained from commercial tylosin, produced by Sinochem Corporation. Their chemical structure and properties were given in Table 1. KH_2PO_4, K_2HPO_4, KOH and HCl used for the preparation of buffer solutions were of reagent grade and were supplied from Biochem, Chemopharma. Analytical-grade organic solvents were used for ultra high performance liquid chromatography analysis. All solutions were prepared with distilled water (resistivity of 2 MΩ cm).

Photocatalyst characteristics

The used photocatalyst medium was provided by Ahlström Paper Group (referenced as Media 1049). It is a commercial non-woven paper composed of cellulosic fibers coated with a mixture of TiO_2 (Millennium PC 500) and SiO_2 as an inorganic binder. It has a specific area of 317 $m^2\ g^{-1}$, a pure anatase crystal structure and 1:1 TiO_2/SiO_2 mass ratio (from manufacturer data). The quantity of catalyst deposited on the media is equal to 25.5 g m^{-2}. Addition of SiO_2 can increase the functionality of TiO_2. Silica acts as a protector between the fibers and the titanium dioxide. Moreover, silica is transparent to UV, and resists to UV radiation and photocatalysis (Petit et al., 2007, Lhomme et al., 2008).

Photoreactor and procedure

Photocatalysis experiments were carried out using a continuous tubular photoreactor with a recirculation system (Figure 1). It consists of a stainless-steel column reactor with a cylindrical cross-section (0.62×10^{-2} m^2) and an internal volume equal to 1.1 L. The photocatalyst media was placed in filtering arrangement (dead-end filtration), between the stainless-steel support and the column in both top and bottom of the reactor. The two sheets of TiO_2-coated paper (corresponding to 0.32 g of TiO_2) were renewed for each set of experiments. The solution to be treated was pumped from an open tank of 2 L capacity under the studied flow rate. An adjustable circulating flow was provided by the mean of a flowmeter and a peristaltic pump. The solution inside the tank was magnetically stirred to keep the solution homogeneous.

A UV-lamp Philips PL-S 9W/10/4P (λ_{max}= 365 nm) was used as light source. It is placed in a Pyrex jacket and crosses perpendicularly the middle of the reactor. The lamp was totally

immersed in the reactor and therefore the maximum light irradiation was achieved. The incident photon flux is equal to 40 ± 0.2 W m^{-2}.
In this work, initial concentration (C_0) of the substrate was set in the range of 10-80 mg L^{-1}. The fact that this concentration is higher than typical environmental values would not induce any change in the reaction mechanism, or in the reaction products (Santaballa et al., 2006).
Prior the photodegradation tests, the solution is flowing for 30 min in the dark in order to reach the adsorption/desorption steady state. Then the lamp is switched on to initiate the irradiation and the photocatalysis processes for 300 min. Samples were taken regularly to evaluate the remaining target compound concentration. The pH and temperature of the solution were also monitored during the runs (WTW inoLab level 1 electrode).
A series of experiments were also conducted in batch mode, in order to investigate the photolytic elimination of the target molecules. No evidence of this phenomenon was observed under the operating conditions.
Moreover, it will be noticed that all experiments were carried out in duplicate and the error is less than 5.0%.

Analysis

Solution samples were taken over irradiation time and filtered through 0.45 µm PTFE Millipore syringe filter prior to analysis. SPM and TYL residual concentrations were monitored by ultra high performance liquid chromatography (UHPLC, Acquity Hclass: Waters), equipped with a photodiode-array detector. Chromatographic separation was performed with a BEH C18 reversed phase column (100 mm × 2.1 mm i.d.× 1.7 µm), at 30 °C and isocratic elution. The mobile phase consisted of 0.1% of aqueous formic acid in acetonitrile/ultra-pure water (20:80 v/v). The injection volume and flow rate were 10 µL and 0.4 mL min^{-1}, respectively. Analytes were detected at a λ_{max} of 232 (SPM) and 290 nm (TYL). The total organic carbon (TOC) was measured by using a Shimadzu 1010 Analytical TOC analyzer.

RESULTS AND DISCUSSION

The degradation kinetics of the target compounds have been analyzed using a pseudo first-order kinetic model (Gaya and Abdullah, 2008), which can be expressed as:

$$Ln\left(\frac{C_0}{C}\right) = k_{ap}.t \qquad (1)$$

C_o and C (mg L^{-1}) were the concentration of pollutant at t =0 and t respectively. The apparent rate constant (k_{ap}, min^{-1}) is given by the slope of the plot of $\ln(C_o/C)$ versus time (t, min) for the first 30 min of reaction.

pH effect

Generally, the degradation rate varies with the solution pH, due to the surface properties of catalyst and ionization (pKa) of organic pollutant. It has been reported that TiO_2 at its pure anatase crystalline form, possesses an amphoteric surface and its point of zero charge (PZC) is at pH 6.3 (Parsons, 2004). For the used media, SiO_2 binder affects the PZC of the catalyst. Indeed, it was shown that pH of the point of zero charge decreases to a value of 3 when the titanium dioxide is supported on silica (Aguedach et al., 2005). Consequently, the surface of the photocatalyst is positively charged at pH < 3 and negatively charged at pH > 3.

The experiments were performed over the pH range (3 - 10) and all the other parameters were maintained constant. A maximum removal rate of about 80% was found at natural pH (corresponding to dissolved pollutant) for both SPM (pH~5.98) and TYL (pH~5.36) after 300 min of reaction. It can be observed that pH highly affects the SPM and TYL degradations which were much faster in acidic media than alkaline solution (Figure 2). In fact, the rate constant k_{ap} declines slightly under acidic conditions (pH~3) for both macrolides, while under alkaline conditions it decreases more strongly for SPM than for TYL.
This difference between the behavior of two antibiotics can be attributed to their pKa (pKa_{SPM} > pKa_{TYL}). For the considered pollutants, the high pKa suggests a high degree of ionization under acidic conditions.

For acidic pH, the adsorption of SPM and TYL on TiO_2-coated paper was facilitated by electrostatic attraction between the negatively charged photocatalyst surface and molecules cations. On the other side, at pH>pKa, the decrease in the degradation rate (SPM~7% and TYL~44%) could be attributed to the electrostatic repulsion due to the negative charge of ionized molecules (deprotonation). In addition, $OH^{\bullet}$ radicals may be scavenged (Sakkas et al., 2007) and do not have the opportunity to react with pollutant molecules. The same tendency concerning pH influence has been reported by several authors (Haque and Muneer, 2007; Gad-Allah et al., 2011).
Consequently, acidic pH was more favorable for the photocatalytic degradation of SPM and TYL using CTCPP due to the higher adsorption of antibiotic molecules on TiO_2-coated paper. A natural pH~6 seems to be the optimum for the degradation of both macrolides molecules.

Effect of initial concentration and application of L-H model

The effect of initial substrate concentration on the photocatalytic degradation efficiency was investigated in the range of 10-80 mg L^{-1}, at a constant flow rate of 0.35 L min^{-1} and natural pH. The removal rate of SPM and TYL decreases respectively from 90.8% and 83.6% to 65.5% and 41% after 300 min of reaction when increasing the initial concentration from 10 to 80 mg L^{-1} (Figure 3). As expected, a maximum degradation was observed at low concentrations in pollutant (10 and 20 mg L^{-1}) and the rate constant decreased with increasing initial concentration. This result can be explained by adsorption/desorption competition between the macrolide molecules and the degradation of intermediates, which may be predominant at high concentrations. In addition, since the amount of photocatalyst and the light intensity are constant in the reactor, the photogenerated oxidative species (primary $OH^{\bullet}$) remain theoretically invariant.

Therefore, although initial macrolide concentration increases and adsorbed amount of macrolide on active surface of photocatalyst enhances, the degradation rate decreases due to a lower $OH^{\bullet}$/pollutant ratio. In addition, the reduction of light penetration due to the increasing of initial concentration leads to less reactive sites creation (Merabet et al., 2009; Li et al., 2015).

Numerous investigations have demonstrated that heterogeneous photocatalysis of organic substrates could be described by L-H kinetic model (Yang et al., 2008; Merabet et al., 2009; Gad-Allah et al., 2010; Laoufi et al., 2013). This kinetic model is commonly used to rationalize the mechanisms of reactions occurring on solid surfaces (Kumar et al., 2008). If we note r_0 (mg L^{-1} min^{-1}) the degradation rate, L-H model can be expressed as follows:

$$r_0 = -\frac{dC_0}{dt} = \frac{K_L\, k_{LH}\, C_0}{1 + K_L\, C_0} \quad (2)$$

where $k_{L\text{-}H}$ (mg^{-1} L min) refers to apparent L-H rate constant and K_L (L mg^{-1}) to the adsorption/desorption equilibrium constant. The linearization form of L-H model leads to:

$$\frac{1}{r_0} = \frac{1}{k_{LH}\, K_L} \cdot \frac{1}{C_0} + \frac{1}{k_{LH}} \quad (3)$$

The values of k_{LH} and K_L constants were determined by linear regression of the plot $1/r_o$ versus $1/C_o$ (Figure 4). The obtained values for SPM (k_{LH} = 1.413 mg^{-1} L min, K_L = 0.0037 L mg^{-1}) and TYL (k_{LH} = 0.5128 mg^{-1} L min, K_L = 0.0136 L mg^{-1}) were of the same order of magnitude than those reported in the literature for the antibiotics photodegradation (Gad-Allah et al., 2011; Dimitrakopoulou et al., 2012). It also appears that SPM degraded faster than TYL and the kinetic reaction step is considered to be the limited step.
These results confirm that L–H model is suitable to describe the kinetic of SPM and TYL degradation using the CTCPP under the investigated conditions.

Effect of flow rate

The effect of flow rate on the degradation efficiency of both SPM and TYL was also studied. The operating values of investigated flow rates were in the range of 0.2-0.55 L min^{-1}. The obtained profiles are summarized in Figure 5. After 300 min of reaction, the maximum k_{ap} value (0.0086 min^{-1} for SPM and 0.0066 min^{-1} for TYL) and maximum removal efficiency (~80 %) were achieved under 0.35 L min^{-1} optimum flow rate.

In the case of any continuous-flow photoreactor, the flow rate is considered as an important factor that affects photocatalytic reaction by changing the convective mass transfer and residence time in the reactor. Convective mass transfer is the more predominant factor that influences the photocatalytic reaction at low flow rate, while residence time is the primary limiting factor at high flow rate (Li et al., 2014).

Up to 0.35 L min^{-1}, the enhancement of degradation efficiency with increasing flow rate indicates that convective mass transfer is the primary limiting factor and then, the diffusion between macrolide and photocatalyst is improved in both SPM and TYL degradation.
Beyond 0.35 L min^{-1}, increasing flow rate leads to lowering the degradation efficiency. In this work, residence time should not play a significant role as we are in the case of circulating reactor. May be hydrodynamic flow regime can play a role. This aspect will be investigated later in the RTD study.

Mineralization of target macrolides

In this work, the extent of the antibiotics mineralization was determined by measuring the total organic carbon in the reaction system. Figure 6 presents the comparison between percentages of TOC removal for four different initial pollutant concentrations after 300 min of irradiation. We note that for lower concentrations, over than half of the initial SPM content and about 35% for TYL have been mineralized after a treatment time of 5 h. At that time, both antibiotics were almost at their maximum abatement.
Further, the obtained values lead us to confirm the presence of organic intermediates generated during the photocatalytic process which compete for adsorption and subsequent photocatalytic degradation. However, the complete mineralization was not achieved for the

considered experimental time duration. It could be supposed that by increasing the irradiation time, most of the reaction by-products would be transformed into inorganic substances such as CO_2 and H_2O.

In addition, both target pollutants have a complex molecular structure which leads to hard mineralization. The difference between mineralization efficiencies of SPM and TYL strongly depend on their molecular structure. Indeed, SPM which has a relatively lower molecular weight than TYL achieved the maximum mineralization (55%).

RTD studies and characterization of flow pattern

In order to well analyze the effect of flow rate on removal efficiency and characterize the liquid flow pattern, RTD studies were carried out for forth-selected values of flow rate (0.25, 0.35, 0.45, 0.55 L min^{-1}).

The residence time distribution was evaluated using E(t) variation with time at the exit of reactor. In this work, KCl was chosen as a tracer (Gholami et al., 2012).
In order to investigate the effect of flow rate on the RTD performance more closely, RTD curves are plotted versus time for each flow rate as shown in Figure 7. E(t) function is expressed as follows:

$$E(t) = \frac{C_i}{\int_0^\infty C\,dt} \tag{4}$$

where C_i is tracer concentration at the exit time t.
As a consequence, the mean residence time ($\bar{t}_m$), the variance of the residence time (σ^2) and the dimensionless variance (σ_D^2) are calculated from the following equations and the results are summarized in table 2:

$$\bar{t}_m = \int_0^\infty tE\,dt \cong \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \tag{5}$$

$$\sigma^2 = \int_0^\infty (t - \bar{t}_m)^2 E\,dt = \frac{\sum (t - \bar{t}_m)^2 C_i \Delta t_i}{\sum C_i \Delta t_i} \tag{6}$$

$$\sigma_D^2 = \left(\frac{\sigma}{\bar{t}_m}\right)^2 \tag{7}$$

It could be observed that the increase in flow rate results in a decrease of $\bar{t}_m$ in the reactor. Generally, $\bar{t}_m$ is the most common parameter of concern and is an indicative of the average transient time of processing material. A lower value of $\bar{t}_m$ indicates higher mean velocity of the flowing material.

In addition, the RTD dimensionless variance (σ_D^2) can be considered as a measure of the dispersion. A lower value of σ_D^2 ($\sigma_D^2 \to 0$) indicates lesser dispersion and the flow approaches to near plug flow. On the other hand, a higher value of σ_D^2 indicates higher dispersion and the flow approaches to perfectly mixed flow (Khataee et al., 2010).

In order to characterize the RTD quantitatively in the photoreactor, the single parameter model was chosen in this work: the tanks-in-series model, where the real circulation loop is

replaced by a series of consecutive, equal volume of ideally stirred tank reactors, resulting in the same longitudinal mixing effect. The degree of mixing is characterized by the number of equivalent stirred tank reactors (N_{eq}) and could be calculated according to Eq. (8).

$$N_{eq} = 1/\sigma_D^2 \quad (8)$$

We note that experimental reactor can be represented by a series of 3 to 5 mixed reactors.
Increasing flow rate within the studied range doesn't considerably affect the flow regime into the reactor. It appears that 0.25 L min^{-1} flow rate is the optimum value corresponding to lowest dispersion. The flow regime is close to plug flow.
Thus, considering the maximum removal efficiency of both SPM and TYL (~80 %), and also the determined flow characteristics and RTD studies, the value of 0.35 L min^{-1} appears to be the optimum flow rate in the case of the studied CTCPP.

This good performance of our experimental reactor can be due to the hydrodynamic behavior of the process. Indeed, RTD experiments show that experimental reactor can be represented by at least 4 stirred reactors in series. For a first order reaction, the presence of stirred reactor in series leads to better degradation rate (Fogler, 1998).

Evaluation of electrical energy per order (EE/O)

The electrical energy consumption has been proposed as a figure-of-merit for comparing the cost of each AOPs technology. Bolton et al. (2001) defined the electric energy per order (EE/O) to use at the first-order kinetic regime at the low pollutant concentrations. It is defined as the number of kilowatt hours of electrical energy required to reduce the pollutant concentration by 1 order of magnitude per $1m^3$ of contaminated water. Assuming first-order kinetics, EE/O (kWh m^{-3} $order^{-1}$) can be calculated from the following equation for a batch reactor:

$$\frac{EE}{O} = \frac{P \times t \times 1000}{V \times 60 \times \log\left(C_i/C_f\right)} \quad (9)$$

where P(kW) is the power of the AOP system, t (min) the irradiation time, V (L) the treated solution volume, C_i and C_f are the initial and final pollutant concentrations, respectively.

The calculated EE/O values for SPM and TYL photodegradation in the optimal conditions (C_0 = 10 mg L^{-1}, Flow rate = 0.35 L min^{-1}, natural pH) were 20.09 and 26.18 kWh $m^{-3}order^{-1}$ respectively. These values showed that the studied system offered the best energetic efficiency compared to those reported in other studies (Table 3).
The obtained data clearly showed that, at optimal operating conditions, the studied reactor presents a better degradation efficiency and energy consumption.

Study of the stability of the photocatalyst media

For ROPs treatment in water, repetitive operation performance is one of the most important parameters for practical application of any developed photocatalytic reactor, to reduce the cost implications (Li et al., 2014). A catalyst reuse study was conducted to determine the stability

of TiO_2-coated paper over nine catalytic cycles. Experiments were carried out for TYL over 300 min in each cycle. As shown in Figure 8, about 80% of TYL was decomposed after 9 cycles of catalyst use. A low degradation removal was recorded in the first uses of the photocatalyst (46.7% and 62.3% for the 1st and 2nd cycle respectively). This lack in the degradation efficiency is probably due to the presence of impurities on the surface of the TiO_2-coated paper which disappear with its reuse. Furthermore, it can be seen that the photocatalytic activity of the catalyst increases (up to 77.8%) after the third catalytic cycle. Even after nine cycles, the immobilized photocatalyst preserves its performance and the apparent rate constant remains high (Figure 8).

These results demonstrate that the used photocatalyst have high catalytic stability which leads to the good reproducibility of the reactor for macrolides degradation. The high repetitive operation performance, as well as the high photocatalytic efficiency and the low energy consumption, makes the CTCPP a promising alternative for the degradation of macrolides in water.

CONCLUSIONS

In this work, the degradation efficiency of SPM and TYL in a circulating TiO_2-coated paper photoreactor (CTCPP) was investigated under some operating conditions such as low power UV-lamp, immobilized catalyst, different pH, initial pollutant concentration and flow rate. The developed photoreactor system shows high degradation efficiency, low energy consumption and good repetitive operation performance for photocatalytic removal of macrolide antibiotics in water. The conclusions based on the experimental results can be summarized as follows:

1. The optimal determined conditions were an initial pollutant concentration lower than 20 mg L^{-1}, 0.35 L min^{-1} flow rate and natural pH solution. Application of L-H model revealed that photocatalytic degradation is reaction step limited.
2. The mineralization of both antibiotics was not complete even at high catalyst photoactivity. The difference between mineralization efficiencies of antibiotics strongly depends on their molecular structure. Further studies on the determination of photodegradation pathway of both SPM and TYL and their formed by-products are under progress.
3. RTD analysis showed that experimental reactor can be represented as a 4 tanks in series. This leads to better degradation performance and energy consumption.
4. The stability of the photocatalyst media has been attested. Nine repetitive catalytic cycles have not altered the efficiency of the photocatalyst.

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Figures captions

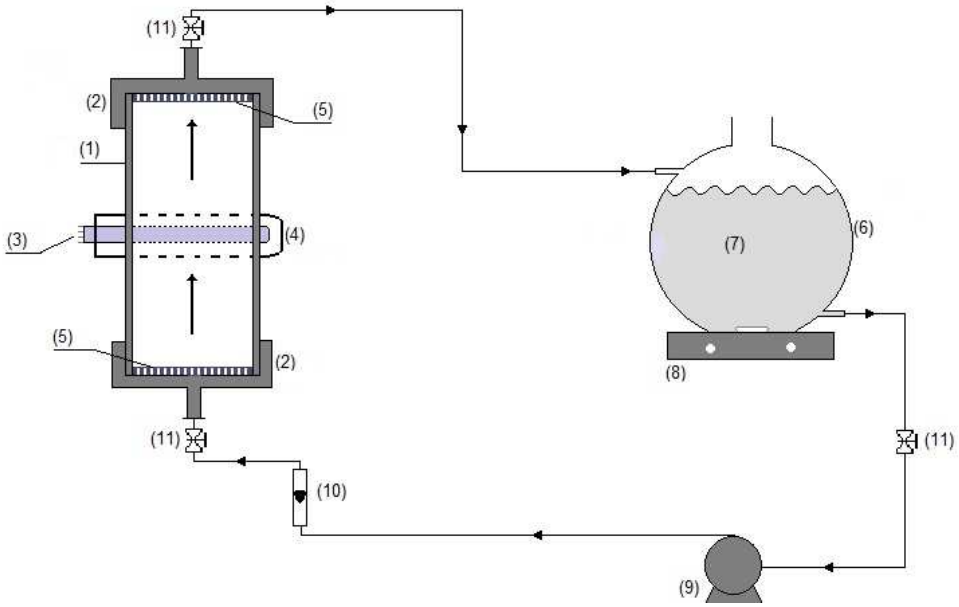
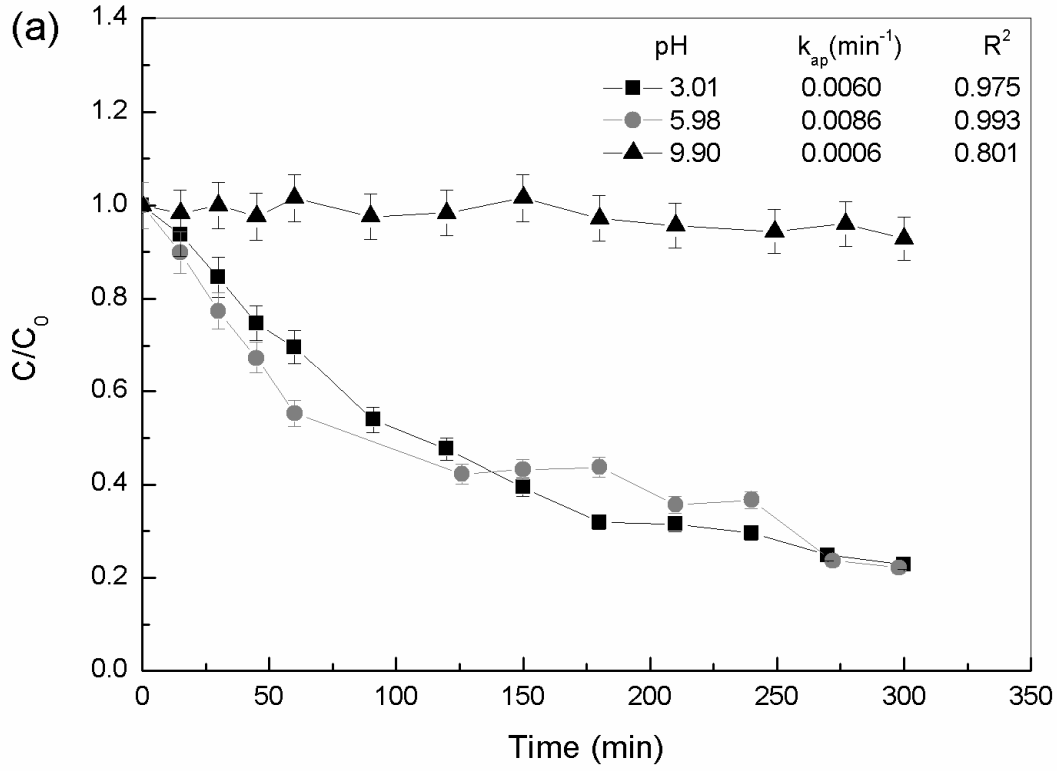


Figure 1. Experimental set-up: (1) column; (2) support; (3) UV lamp; (4) pyrex tube; (5) catalyst paper; (6) tank; (7) solution; (8) magnetic stirrer; (9) peristaltic pump; (10) flowmeter; (11) valve.


(a)
pH
$k_{ap}(min^{-1})$
R^2
3.01 0.0060 0.975
5.98 0.0086 0.993
9.90 0.0006 0.801
C/C0
Time (min)

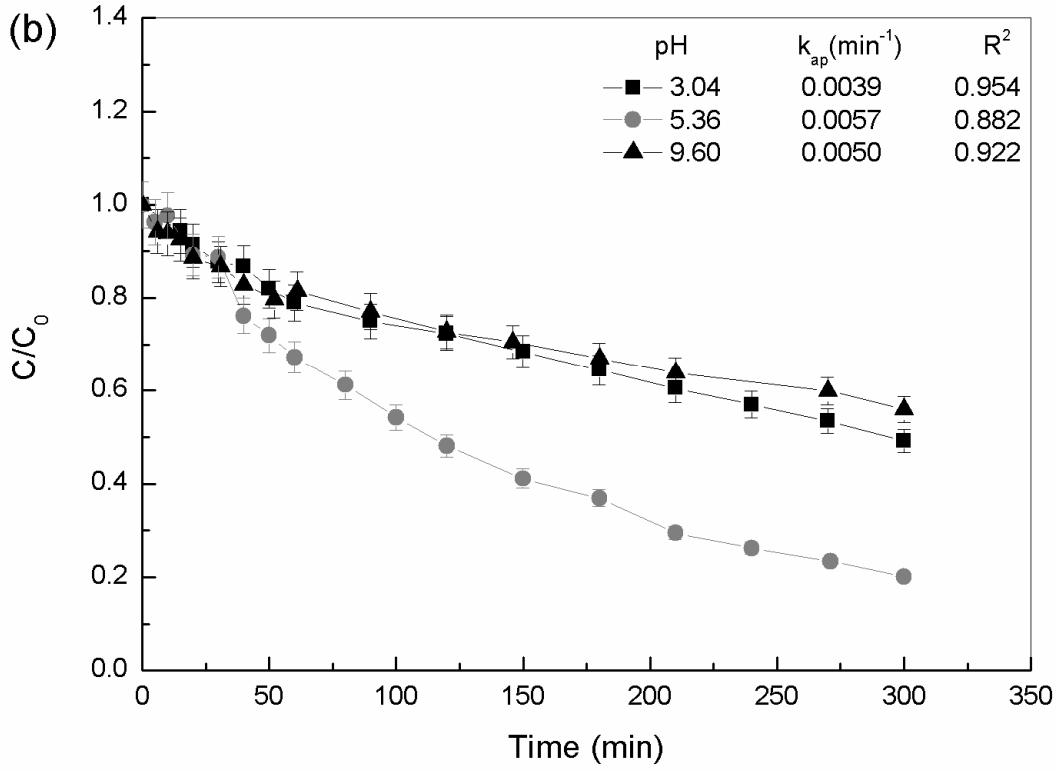
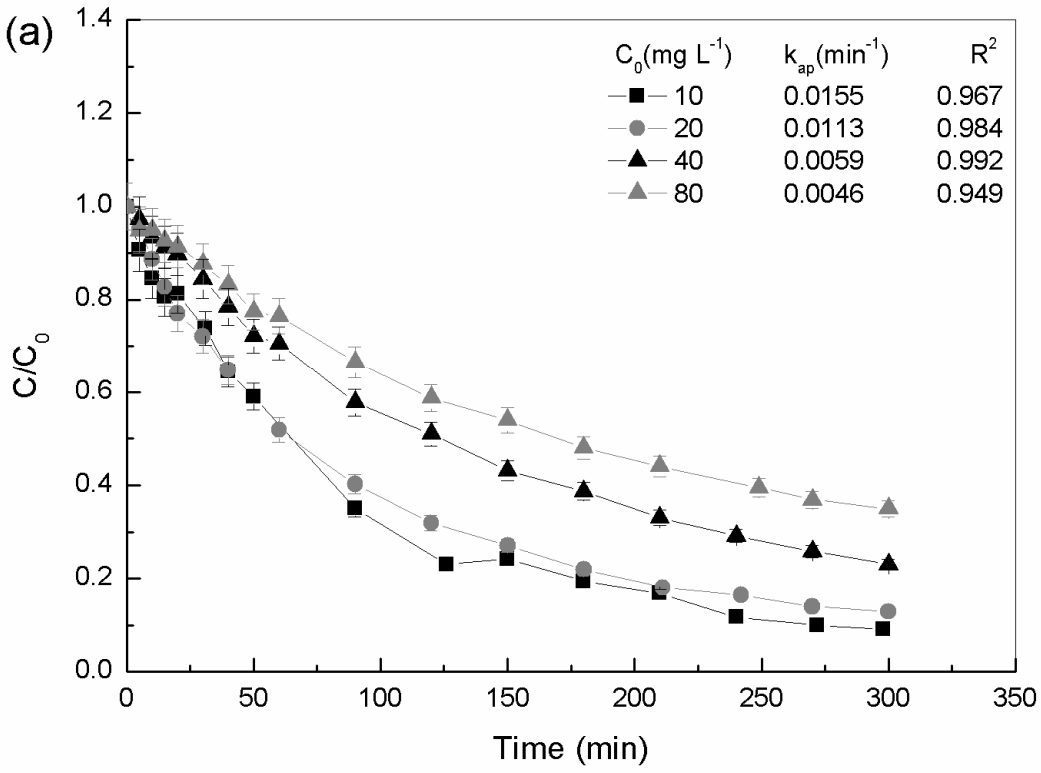

(b)
pH
$k_{ap}(min^{-1})$
R^2
3.04 0.0039 0.954
5.36 0.0057 0.882
9.60 0.0050 0.922
C/C0
Time (min)

Figure 2. Effect of pH on the photocatalytic degradation: (a) SPM ; (b) TYL,(C_0 = 10 mg L^{-1}, Flow rate: 0.35 L min^{-1}).



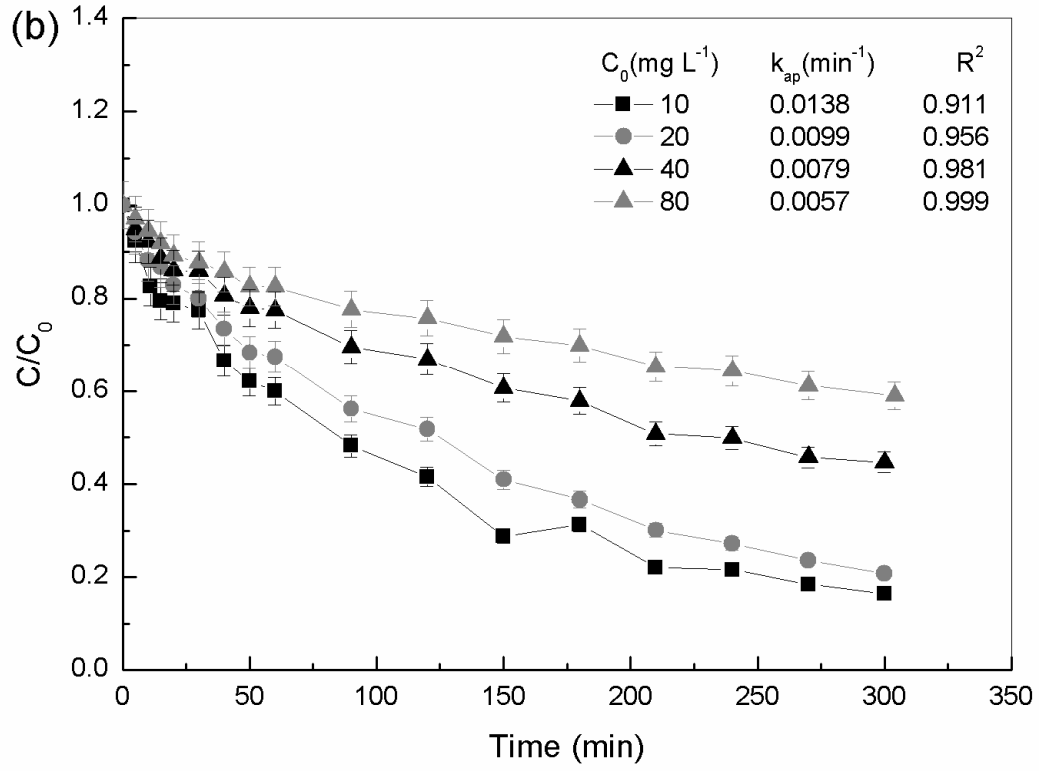


Figure 3. Effect of initial concentration on the photocatalytic degradation: (a) SPM ; (b) TYL, (natural pH, Flow rate : 0.35 L min^{-1}).

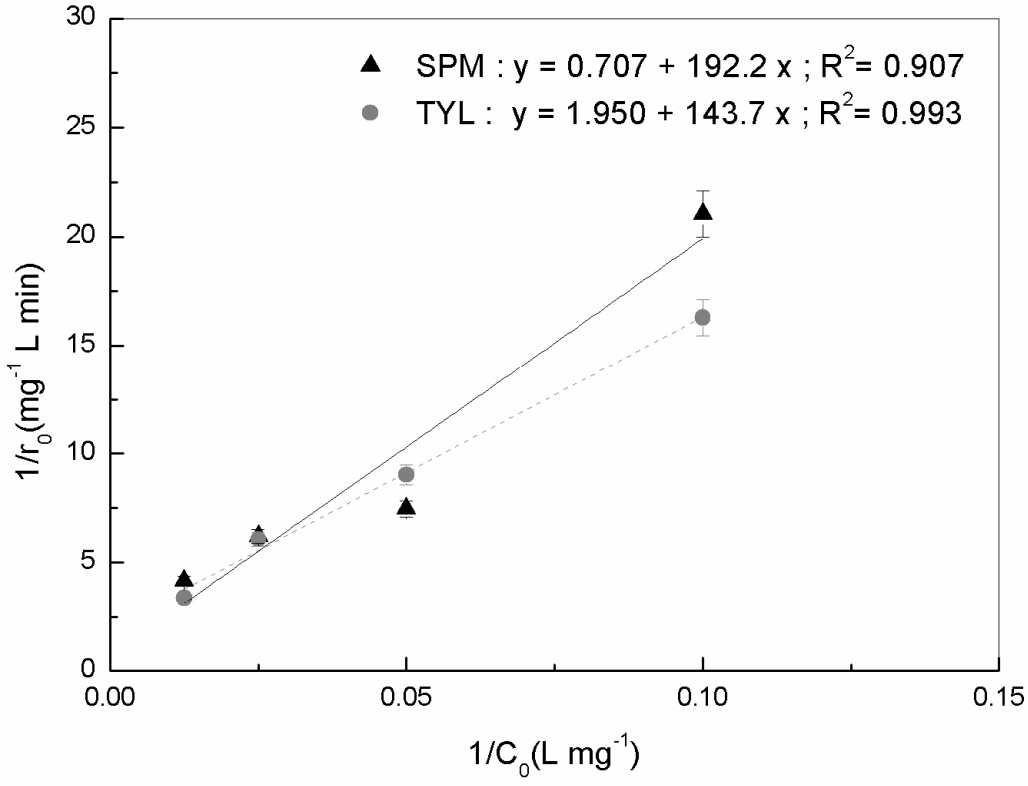
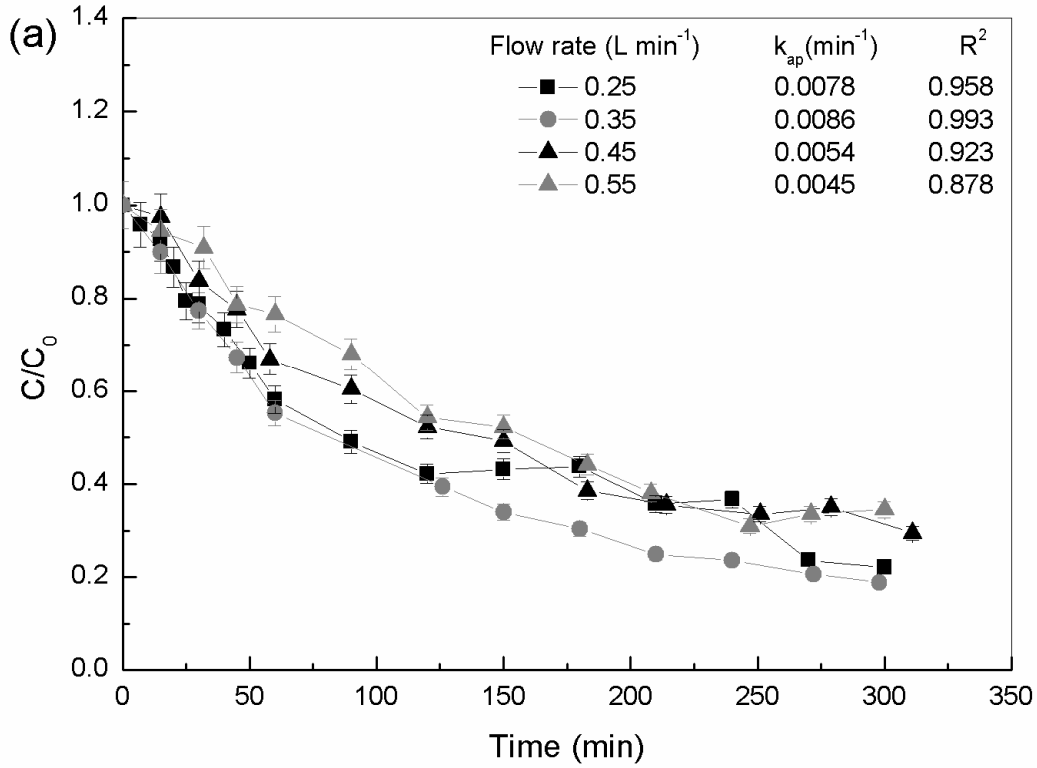


Figure 4. Determination of L-H model constants for SPM and TYL degradation.


(a)
Flow rate (L min-1)
kap(min-1)
R2
0.25 0.0078 0.958
0.35 0.0086 0.993
0.45 0.0054 0.923
0.55 0.0045 0.878
C/C0
Time (min)

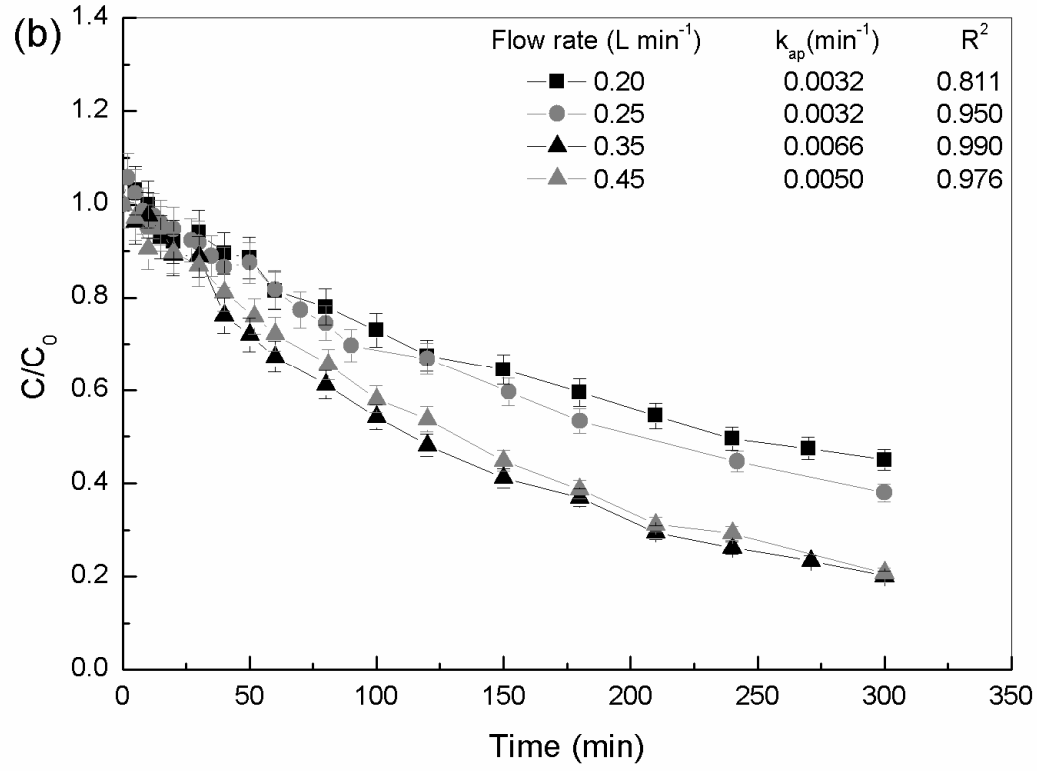

(b)
Flow rate (L min-1)
kap(min-1)
R2
0.20 0.0032 0.811
0.25 0.0032 0.950
0.35 0.0066 0.990
0.45 0.0050 0.976
C/C0
Time (min)

Figure 5. Effect of flow rate on the photocatalytic degradation: (a) SPM ; (b) TYL, (natural pH, C_0 = 10 mg L^{-1}).

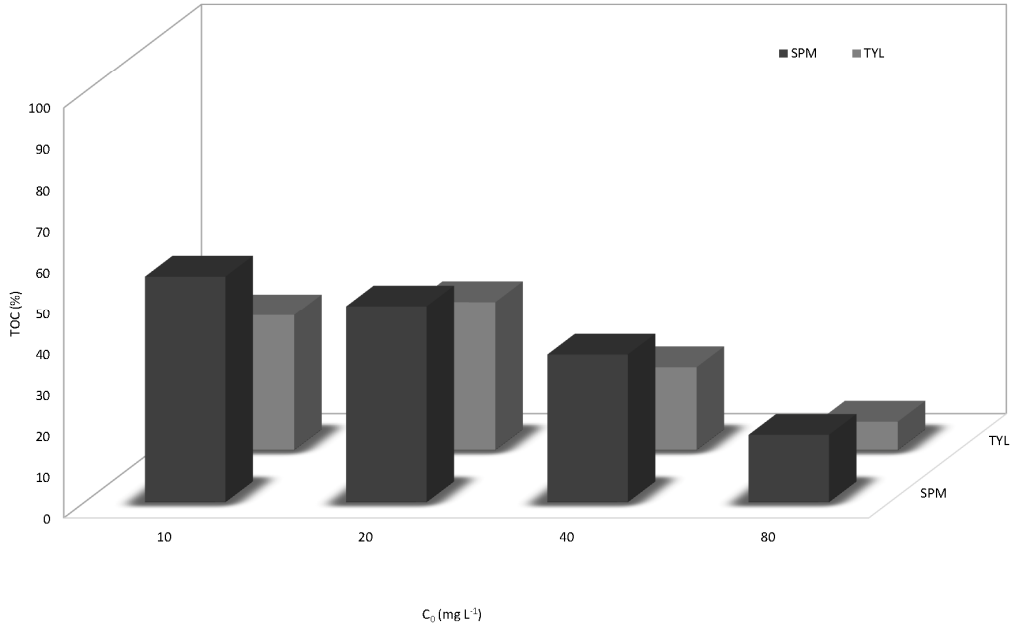


Figure 6. Mineralization efficiency of macrolides versus initial pollutant concentration.

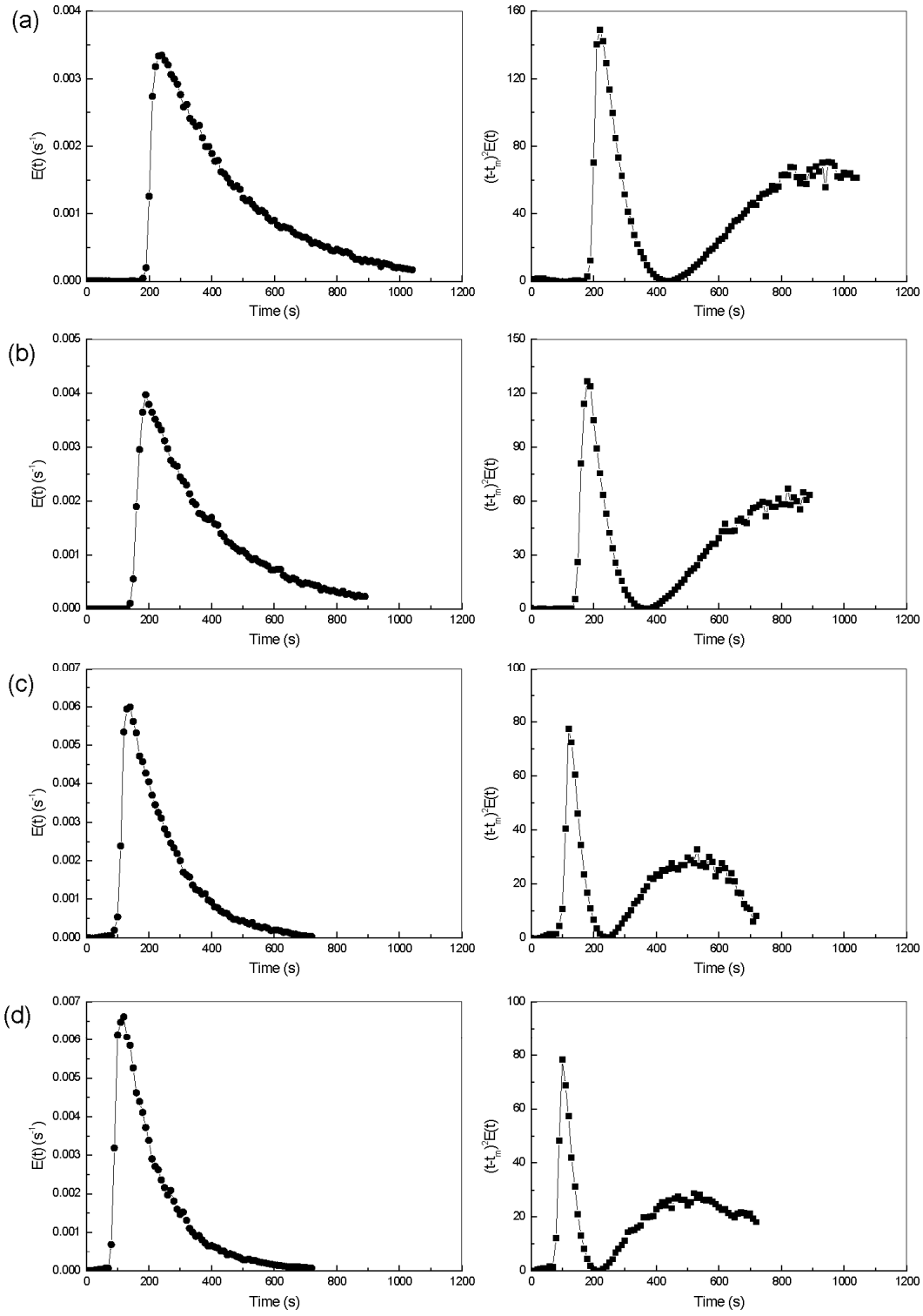
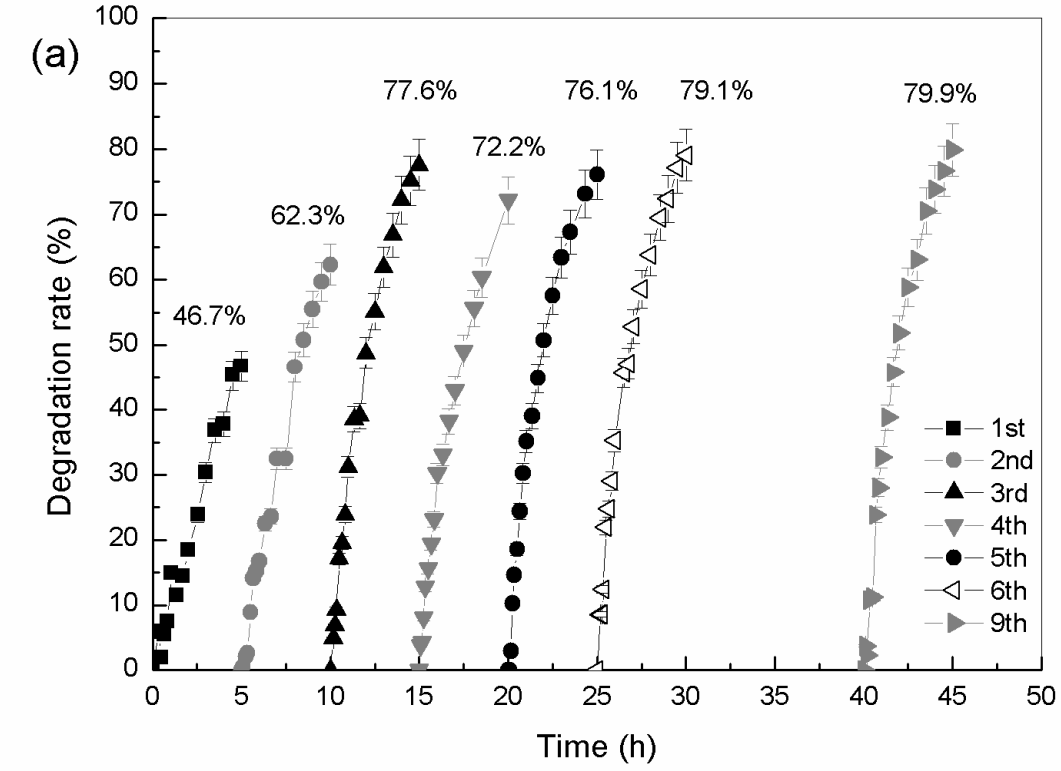


Figure 7. Typical RTD curves at different flow rates. (a) 0.25; (b) 0.35; (c) 0.45 and (d) 0.55 L min^{-1}


(a)
Degradation rate (%)
Time (h)
46.7%
62.3%
77.6%
72.2%
76.1%
79.1%
79.9%
1st
2nd
3rd
4th
5th
6th
9th

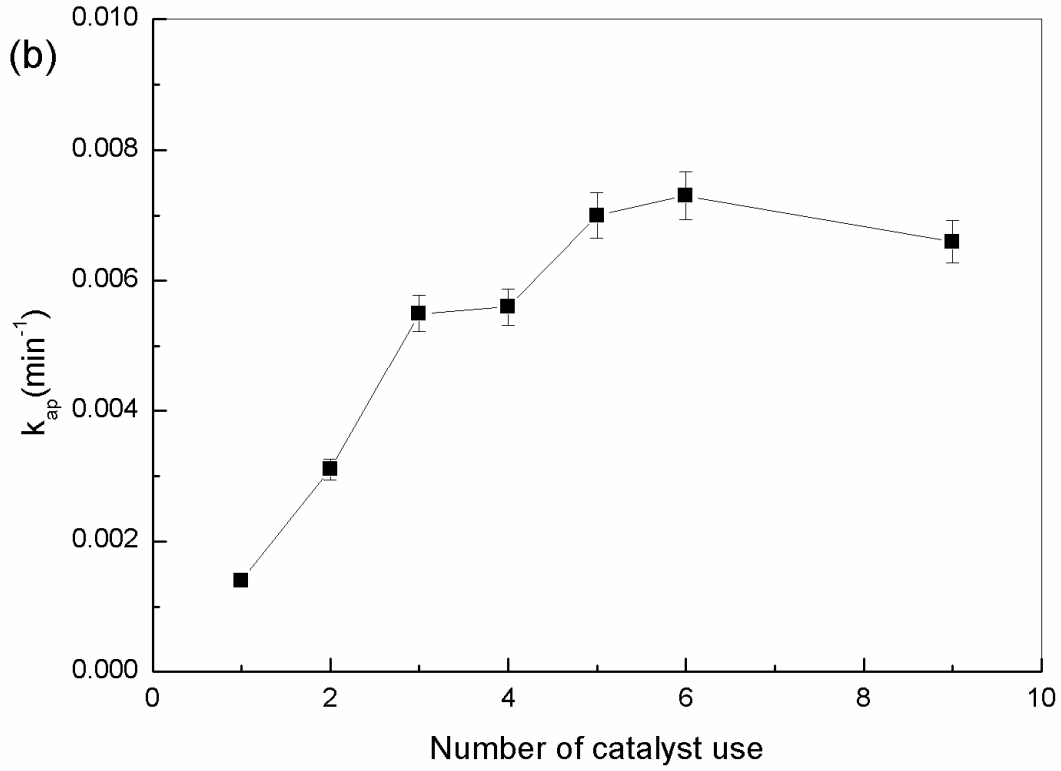

(b)
k_{ap}(min^{-1})
Number of catalyst use

Figure 8. Reuse of the TiO_2-coated paper: (a) Removal rate evolution (b) Kinetic constant evolution, (C_0 = 10 mg L^{-1}, natural pH, flow rate = 0.25 L min^{-1}).

Tables

Table 1. Physicochemical properties and characterization of SPM and TYL

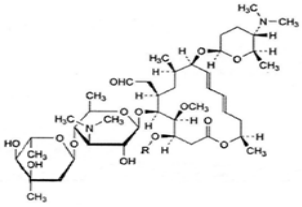
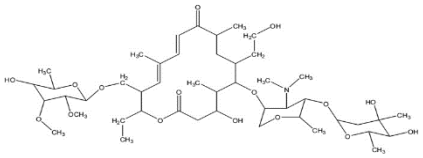
Compound/group	Spiramycin/macrolide	Tylosin/macrolide
Use	Antibacterial for human and veterinary medicine	Antibacterial for veterinary medicine
CAS number	24916-50-5	1401-69-0
Mw (g mol^{-1})	843.1	916.1
Formula	$C_{43}H_{74}N_2O_{14}$	$C_{46}H_{77}NO_{17}$
Structure		
Solubility in water (mg L^{-1})	Little	50000
pKa	8	7.1
Melting point (°C)	134-137	135-137
Color	White or slightly yellowish powder	Off-white to pale yellow solid

Table 2. Characteristic parameters of flow regime

Flow rate (L min^{-1})	$\bar{t}_m$ (min)	σ_D^2	N_{eq}
0.25	7.27	0.204	4.89
0.35	6.11	0.225	4.43
0.45	4.01	0.231	4.33
0.55	3.55	0.305	3.28

Table 3. Electrical energy per order (EE/O) for some reported photoreactors in the case of pharmaceuticals photocatalytic degradation

Pollutant	Photoreactor	EE/O (kWh m^{-3})	Reference
Paracetamol	TiO_2 suspension photoreactor	560.76	Yang et al., 2008
Tylosin	TiO_2 suspension photoreactor	468.61	Laoufi et al., 2013
Amoxicillin	TiO_2-coated beads photoreactor	1.97×10^5	Li et al., 2015